

Phase Equilibria in the System Vanadium Oxide-Niobium Oxide

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The phase diagram for the pseudo-binary system V_2O_5 – Nb_2O_5 was constructed from fusion characteristics and x-ray diffraction data. Three compounds were postulated for the system. The compound VNb_9O_{25} and $V_3Nb_{23}O_{62}$ were found to melt incongruently at about 1290 °C and 1322 °C respectively. The third compound occurring at about 93 to 94 mole percent Nb_2O_5 melted incongruently at approximately 1332 °C. Apparently, Nb_2O_5 accepted up to 5 mole percent V_2O_5 in solid solution, however, V_2O_5 did not accept any appreciable Nb_2O_5 in solid solution.

In addition, the Nb_2O_5 rich portions of the following binary systems were reinvestigated: ZnO – Nb_2O_5 , NiO – Nb_2O_5 , Al_2O_3 – Nb_2O_5 , TiO_2 – Nb_2O_5 , and ZrO_2 – Nb_2O_5 . In each case an Nb_2O_5 solid solution had been reported previously in excess of 90 mole percent Nb_2O_5 . However, subsequent data indicated that these Nb_2O_5 solid solutions contained discrete compounds which are related to those found in the pseudo-binary V_2O_5 – Nb_2O_5 .

1. Introduction

In a number of previously reported phase studies of the general type M_xO_y – Nb_2O_5 , the existence of Nb_2O_5 -rich solid solutions were postulated. These include TiO_2 – Nb_2O_5 , ZrO_2 – Nb_2O_5 [1],¹ Al_2O_3 – Nb_2O_5 [3, 4], ZnO – Nb_2O_5 [2] and NiO – Nb_2O_5 [3, 4].

When selected compositions in these systems were examined they were found to give x-ray powder diffraction patterns with marked similarity one to the other as well as to the stable high temperature form of Nb_2O_5 .

However, it seemed unlikely that a solid solution with oxygen deficiencies could account for the differences in the x-ray pattern. In an attempt to determine whether these phases were solid solutions or discrete compounds the system V_2O_5 – Nb_2O_5 was selected to be studied, as cations of similar ionic radii and the same valence might be most expected to form a solid solution.

Goldschmidt [3] surveyed and reported the existence of two intermediate phases in the system: $\beta'(Nb, V)_2O_5$ and a phase with a rutile-type structure, $a=4.633$ Å, $c=3.021$ Å. However, no systematic attempt to study the phase equilibrium relationships in air has been previously reported.

X-ray diffraction data, together with the determination of the melting points of the compounds and the solidus and liquidus temperatures at various compositions across the system have supplied data from which an equilibrium diagram has been constructed.

2. Sample Preparation and Test Methods

High purity grade niobium and vanadium pentoxides were used. Spectrographic analysis indicated less than 0.1 percent Si, 0.01 percent Fe, Sn, and Ti and 0.001 percent Ca and Mg in the former and less than about 0.01 percent Si, 0.001 percent Ca and Cr and 0.0001 percent Ag, Ca, Mg and Mn in the latter. Cu was not determined in Nb_2O_5 because of Nb interference.

Mixtures of V_2O_5 and Nb_2O_5 were weighed to the nearest ± 0.1 mg in sufficient quantities to yield 2 g batches. No corrections were made for percent purity except loss on ignition. Each batch was mixed in a mechanical shaker for 15 min. The mixtures were then pressed into a disk in a $\frac{5}{8}$ in. diameter mold at 10^4 lb in⁻². The disks were placed on setters fabricated from platinum foil and calcined in air at 500 °C for 10 hr. Following this preliminary heat treatment specimens ranging in composition from 5 to 55 mole percent Nb_2O_5 were recalcined at 600 °C for 168 hr in sealed Pt tubes. Specimens ranging in composition from 90 to 99 mole percent Nb_2O_5 received an additional calcination of 1000 °C for 5 hr.

Since V_2O_5 was found to be volatile only to the extent of about 0.46 percent when heated to about 1000 °C for 6 hr, no correction other than loss on ignition was applied. However, to minimize possible volatility at higher temperatures, sealed platinum tubes were employed for all succeeding experiments unless otherwise stated. At this point it should be noted that platinum tubes approximately 2 cm long were used to contain the specimen. About one-third

¹ Figures in brackets indicate the literature references at the end of this paper.

of the volume was occupied by the specimen and the remainder of the tube was flattened prior to sealing. At elevated temperatures the expansion of the flattened portion of the tube provided the necessary additional volume for expansion of the vapors without rupture.

Sub-solidus and melting point values were obtained by quenching specimens sealed in platinum tubes and examining them at room temperature. An electrically heated vertical tube resistance furnace

was used for quenching which had a primary winding of 60% Pt-40% Rh and a secondary or booster winding of 80% Pt-20% Rh. An a-c controller utilizing the furnace primary as one arm of a Wheatstone bridge served to control the furnace temperature to $\pm 2^\circ\text{C}$ for extended periods of time. The secondary was regulated with a variable auto-transformer.

Temperatures were measured with a Pt versus Pt 10 percent Rh thermocouple which was calibrated

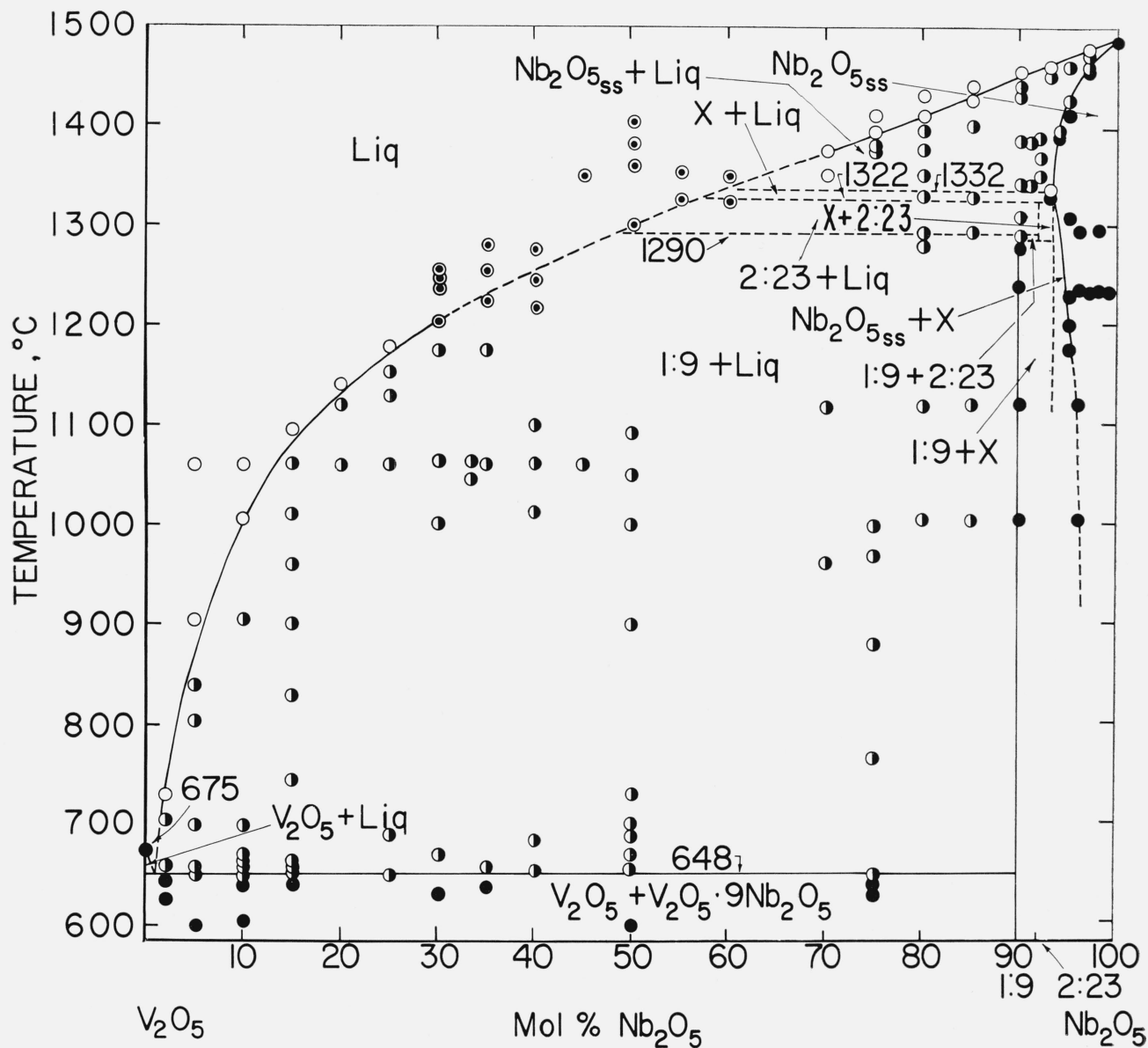


FIGURE 1. Phase equilibrium diagram for the system vanadium oxide-niobium-oxide.

●—no melting.
 ○—partial melting.
 ○—complete melting.
 ⊙—cannot be interpreted from fusion characteristics.
 Liq.—liquid.

X—unknown phase.
 $\text{Nb}_2\text{O}_{5\text{ss}}$ — Nb_2O_5 solid solution.
 For clarity, not all experimental data appearing in table 4 are plotted on this diagram.

several times during the course of the work against the reported values of NaCl (800.5 °C) [6], Au (1063 °C) [5] and barium disilicate (1420 °C) [7].

Liquidus values were established in the following manner: (a) In the region from 2 to 5% Nb₂O₅, the formation of a concave meniscus established the liquidus. (b) In the region from 5 to 30% Nb₂O₅, specimens when quenched from above the liquidus and examined at room temperature were glass. (c) In the region from 30 to 70% Nb₂O₅, no criteria could be employed to establish the liquidus since any given composition between these limits gave the same physical appearance over a range of about a hundred degrees, and this portion (fig. 1) of the curve was dashed. (d) In the region from 70 to 100% Nb₂O₅ (fig. 1) the formation of a concave meniscus and the abrupt change in x-ray diffraction pattern established the liquidus.

The first sign of glazing of the specimen's surface, together with a marked color change established the solidus in the 0–90 mole percent Nb₂O₅ compositional range. This interpretation seemed reasonably valid since most specimens showed abrupt changes in x-ray diffraction patterns when partially melted. Unfortunately, compositions in the Nb₂O₅ rich portion of the system 90–99% Nb₂O₅, did not provide a definitive picture of partial melting, and the approximate solidus values were delineated by data obtained from changes in the x-ray diffraction powder patterns of the quenched specimens and the solidus (figs. 1 and 2) in this region is dashed. The precision of the temperature measurement for the experimental data points is about ±2 °C and the overall accuracy of the reported temperature is about ±5 °C.

Equilibrium is generally considered to have been obtained when x-ray diffraction patterns of specimens successively heated for longer times and/or at higher

temperatures show no change. However, as this system does not appear to be binary at high temperatures this criteria could not always be applied without interpretation. (See sec. 4 and table 4.) X-ray diffraction powder patterns were made using a high angle recording Geiger counter diffractometer and nickel-filtered copper radiation, with the Geiger counter traversing the specimen at 1/4°2θ/min and radiation being recorded on the chart at 1°2θ/in. The unit cell dimensions reported can be considered accurate to about ±5 in the last decimal place listed.

3. Compounds in the Pseudo-Binary System V₂O₅—Nb₂O₅

3.1. V₂O₅

Holtzberg et al. [8] concluded from x-ray diffraction and differential thermal analyses data that V₂O₅ has only one stable form. These results were later independently verified by Levin and McDaniel [9] by high temperature x-ray diffraction analysis. The structure of V₂O₅ was described by Byström et al. [10] as having the space group Pmmn with two molecules per unit cell, and the indexed x-ray powder diffraction pattern was reported by Swanson et al. [11] $a=11.51$ Å, $b=3.559$ Å, $c=4.371$ Å. The melting point of 675 ± 5 °C was established for V₂O₅ by C. L. McDaniel of this laboratory [12].

3.2. Compound V₂O₅·9Nb₂O₅

The compound V₂O₅·9Nb₂O₅ was found to occur in the present study and to be stable to the incongruent melting point at about 1290 °C. Goldschmidt [3] reported a solid solution phase β' (Nb,V)₂O₅ which had a nominal composition Nb_{1.8}V_{0.2}O₅. He reported the unindexed x-ray diffraction pattern of β' (Nb,V)₂O₅. In the present study, the x-ray diffraction powder pattern of V₂O₅·9Nb₂O₅ was found to be essentially the same as that previously reported. The compound V₂O₅·9Nb₂O₅ (table 1) which was indexed on the basis of a body-centered tetragonal cell $a=15.72$ Å, $c=3.821$ Å was found to be isostructural with a series of phases of the general type M₂O₅·9M'₂O₅ [13] and apparently with Ta₂O₅·2Nb₂O₅ which was previously reported by Holtzberg and Reisman [14] as being cubic, and by Mohanty et al. [15] as being tetragonal.

3.3. Compound V₂Nb₂₃O₆₂

A compound was found to occur in the system at the ratio 2V₂O₅:23Nb₂O₅ which exists from about 1284 °C, depending on the length of heating time, to the incongruent melting point at 1322 °C. The indexed x-ray diffraction powder pattern given in table 2 has a marked similarity to that of the high temperature form of Nb₂O₅. However, this phase could not be indexed as a solid solution of the high temperature modification Nb₂O₅. Roth and Wadsley [16] have shown from a single crystal structure determination that a phase TiO₂·12Nb₂O₅ occurs in the system TiO₂—Nb₂O₅ and is a member of a series

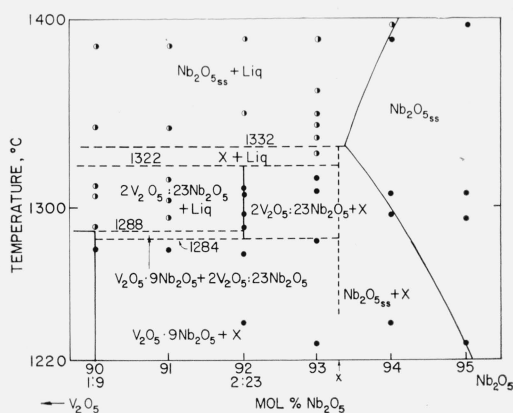


FIGURE 2. Expanded view of the high Nb₂O₅ region of the phase diagram for the system vanadium oxide-niobium oxide.

●—no melting.
○—partial melting.
Li.—liquid.
X—unknown phase
Nb₂O_{5ss}—Nb₂O₅ solid solution.

$M_{3n+1}O_{8n-2}$ with $n=8$. The composition $2V_2O_5 \cdot 23Nb_2O_5$ was found to have an x-ray diffraction powder pattern which is apparently isostructural with $TiO_2 \cdot 12Nb_2O_5$ which could be indexed on the basis of a monoclinic cell $a=29.77$ Å, $b=3.823$ Å, $c=21.05$ Å and $\beta=95^\circ 1.6'$.

The composition $2V_2O_5 \cdot 23Nb_2O_5$ has the general formula $M_{50}O_{125}$. However, the structural formula $M_{3n+1}O_{8n-2}$ (referring to one-half the unit cell) requires the composition to be $M_{50}O_{124}$. From the above considerations it is likely that 1 out of 125 oxygen ions are lost and that the system is not binary.

TABLE 1. X-ray diffraction powder data for the compound $V_2O_5 \cdot 9Nb_2O_5$ (CuK α radiation)

d Obs Å	I/I_0^a	$1/d^2$ obs Å $^{-2}$	$1/d^2$ calc. Å ^{-2}b	hkl^b
11.340	1	0.0080	0.0081	110
7.82	1	.0163	.0162	200
5.54	1	.0326	.0325	220
4.96	25	.0407	.0406	310
3.92	3	.0652	.0649	400
3.70	35	.0729	.0726	101
3.490	100	.0815	.0811	420
3.353	12	.0889	.0888	211
3.076	1	.1057	.1055	510
2.868	30	.1216	.1213	312
2.696	15	.1376	.1375	411
2.482	15	.1623	.1622	620
2.426	5	.1700	.1699	501
2.318	5	.1862	.1862	521
2.222	1	.2025	.2028	710
2.177	1	.2110	.2109	640
2.139	5	.2186	.2186	611
2.062	21	.2353	.2353	730
1.996	1	.2510	.2510	631
1.962	2	.2597	.2596	800
1.910	12	.2742	.2742	002

^a Relative intensity.

^b Based on tetragonal cell, $a=15.72$ Å, $c=3.821$ Å.

TABLE 2. X-ray diffraction powder data for the compound $V_2Nb_{23}O_{62}$ (CuK α radiation)

d Obs Å	I/I_0^a	$1/d^2$ obs Å $^{-2}$	$1/d^2$ calc Å $^{-2}$	hkl
10.48	4	0.0091	0.0092	002
9.04	3	.0125	.0125	202
6.81	3	.0216	.0216	401
5.25	3	.0364	.0364	004
5.09	30	.0387	.0387	204
4.70	20	.0450	.0449	601
3.74	43	.0716	.0716	111
3.60	100	.0772	.0773	801
3.469	80	.0831	.0831	206
3.348	17	.0892	.0892	113
3.273	5	.0933	.0933	605
3.213	5	.0969	.0966	312
3.068	5	.1061	.1062	406
2.839	23	.1241	.1242	313
2.761	17	.1312	.1313	510
2.700	20	.1372	.1372	605
2.620	3	.1459	.1456	712
2.528	27	.1565	.1564	008
2.467	16	.1643	.1642	208
2.310	17	.1874	.1872	10 0 5
2.066	37	.2343	.2344	4 0 10
2.039	38	.2404	.2403	609
1.913	33	.2734	.2736	020

^a Relative intensity.

^b Based on monoclinic cell $a=29.77$ Å, $b=3.823$ Å, $c=21.05$ Å and $\beta=95^\circ 1.6'$.

3.4. Compound X

A new phase was found to occur in the system at approximately 93 to 94 mole percent Nb_2O_5 and to melt incongruently at about 1332 °C. The partially indexed x-ray diffraction powder pattern is given in table 3. The x-ray pattern of this phase has the greatest similarity to the high temperature polymorph of Nb_2O_5 of any of the phases which occur in the system. However, the low angle x-ray diffraction lines, which should shift the least in 2θ for a solid solution, actually are shifted more than many high angle lines. Therefore, the pattern cannot be indexed on the basis of an Nb_2O_5 solid solution or as a solid solution of $V_2Nb_{23}O_{62}$.

TABLE 3. X-ray diffraction powder data for the unknown phase X occurring at about 93 to 94 mole percent Nb_2O_5 (CuK α radiation)

hkl^a	d_{calc} Å	d_{obs} Å	I/I_0^b
002	15.85	16.00	5
003	10.57		
201	10.53	10.57	10
103	10.53		
201	9.09	9.11	6
004	7.93	7.92	6
203	6.57	6.55	6
105	6.54		
006	5.28		
402	5.27	5.27	7
206	5.26		
401	5.26		
400	5.11	5.12	35
107	4.68	4.68	17
402	4.54	4.54	5
404	3.88	3.88	5
308	3.87	3.83	6
010	3.83		
110	3.76		
111	3.76	3.75	65
306	3.75		
502	3.74		
109	3.63	3.63	83
112	3.63		
211	3.53	3.53	10
503	3.53		
009	3.52		
603	3.51	3.51	13
309	3.51		
213	3.492		
601	3.483	3.477	100
114	3.464		
604	3.461		
208	3.419	3.418	15
		3.290	5
		3.190	7
		3.076	8
		2.953	8
		2.834	23
		2.771	32
		2.707	33
		2.626	4
		2.549	13
		2.536	33
		2.514	4
		2.473	27
		2.451	5
		2.335	9
		2.314	16
		2.273	4
		2.259	4
		2.202	4
		2.171	7
		2.102	4
		2.085	21
020		2.040	25
		1.9161	31

^a This pattern was tentatively indexed only after approximate a , c , and β unit cell constants were provided by Mr. A. Perloff from $h0l$ single crystal precession data. The unit cell constants derived from this data are $a=21.12$ Å, $b=3.831$ Å, $c=32.75$ Å and $\beta=104^\circ 5'$. With the exception of the (020) Miller indexes are not reported for reflections with d values less than 3.419 Å because of the relatively large size of the monoclinic cell.

^b Relative intensity.

3.5. Rutile Type Phase

Goldschmidt [3] reported a phase with a rutile type structure and an approximate composition ranging from $90\text{V}_2\text{O}_5:10\text{Nb}_2\text{O}_5$ to about $75\text{V}_2\text{O}_5:25\text{Nb}_2\text{O}_5$. According to Goldschmidt this rutile phase formed from specimens fused in a carbon arc furnace in an atmosphere of argon and was not present when the specimens were annealed at 800°C in air. In the present study no rutile phase was found to occur in the system in an air environment. However, the composition $75\text{V}_2\text{O}_5:25\text{Nb}_2\text{O}_5$ heated to about 1300°C in a flowing stream of argon contained a rutile type phase.

From the above discussion it can probably be concluded the rutile phase is a reduced phase which occurs in the V-Nb-O system.

3.6. Nb_2O_5

The phase equilibrium relations of the polymorphs of Nb_2O_5 have been discussed by various workers [17], [18], [19], [20]. Since it has been concluded by [17], [20], [21] that the high temperature polymorph of Nb_2O_5 is the stable form and since V_2O_5

has no catalytic action on the various modifications of Nb_2O_5 no phase transition has been indicated. The unit cell dimensions were reported previously by one of the present authors [21].

4. Discussion of Phase Equilibria

Although the $\text{V}_2\text{O}_5\text{-Nb}_2\text{O}_5$ system does not appear to be binary, a pseudo-binary phase diagram can be constructed from the experimental data listed in table 4. The appearance of the pseudo-binary diagram might well be changed by different environmental and/or time-temperature experimental conditions and only a complete study of the ternary diagram V-Nb-O could be expected to elucidate the true equilibrium relations. As constructed, the pseudo-binary system contains three intermediate compounds, all melting incongruently. The indexed x-ray diffraction powder pattern and unit cell dimensions of the first, $\text{V}_2\text{O}_5 \cdot 9\text{Nb}_2\text{O}_5$, are given in table 1 and those of the second, $\text{V}_2\text{Nb}_{23}\text{O}_{62}$, in table 2. The d -spacings for the third, a compound of unknown symmetry occurring at about 93 to 94 mole percent Nb_2O_5 , are given in table 3.

TABLE 4. *Experimental data for compositions in the system vanadium oxide-niobum oxide*

Composition		Heat treatment ^a		Results	
V_2O_5	Nb_2O_5	Temp.	Time	Physical observation	X-ray diffraction analysis ^b
<i>Mole %</i>	<i>Mole %</i>	<i>°C</i>	<i>hr</i>		
98	2	627	1	Not melted.....	$\text{V}_2\text{O}_5 + \text{V}_2\text{O}_5 \cdot 9\text{Nb}_2\text{O}_5 + \text{unknown}^c$
		649	0.08	Partially melted.....	$\text{V}_2\text{O}_5^{\text{ss}}^d + \text{V}_2\text{O}_5 \cdot 9\text{Nb}_2\text{O}_5$
		661	.08do.....do.....
		707	.25do.....	$\text{V}_2\text{O}_5^{\text{ss}}^d + \text{unknown}^c$
		730	.33	Completely melted.....	Do.
95	5	600	.3	Not melted.....	$\text{V}_2\text{O}_5 + \text{L} - \text{Nb}_2\text{O}_5^e$
		602	.5do.....	Do.
		652	19	Partially melted.....	$\text{V}_2\text{O}_5 \cdot 9\text{Nb}_2\text{O}_5 + \text{V}_2\text{O}_5^{\text{ss}}^d$
		658	.5do.....	Do.
		700	.5do.....	Do.
		804	.5do.....	$\text{V}_2\text{O}_5^{\text{ss}}^d$
		841	.5do.....	Do.
		904	.5	Completely melted.....	Glass
90	10	1060	1do.....	Do.
		605	.5	Not melted.....	$\text{V}_2\text{O}_5 + \text{V}_2\text{O}_5 \cdot 9\text{Nb}_2\text{O}_5$
		640	.33do.....do.....
		650	20	Partially melted.....	$\text{V}_2\text{O}_5^{\text{ss}}^d + \text{V}_2\text{O}_5 \cdot 9\text{Nb}_2\text{O}_5$
		652	.33do.....do.....
		658	.33do.....	$\text{V}_2\text{O}_5^{\text{ss}}^d + \text{V}_2\text{O}_5 \cdot 9\text{Nb}_2\text{O}_5$
		662	.33do.....	Do.
		664	67do.....	$\text{V}_2\text{O}_5^{\text{ss}}^d + \text{V}_2\text{O}_5 \cdot 9\text{Nb}_2\text{O}_5$
		666	.33do.....	Do.
		673	.08do.....	$\text{V}_2\text{O}_5^{\text{ss}}^d + \text{V}_2\text{O}_5 \cdot 9\text{Nb}_2\text{O}_5$
		700	.5do.....	$\text{V}_2\text{O}_5^{\text{ss}}^d + \text{V}_2\text{O}_5 \cdot 9\text{Nb}_2\text{O}_5 + \text{unknown}^c$
		904	.5do.....	Glass
		1006	.5	Completely melted.....	Do.
85	15	1060	1do.....	Do.
		^f 640	.33	Not melted.....	$\text{V}_2\text{O}_5 + \text{V}_2\text{O}_5 \cdot 9\text{Nb}_2\text{O}_5 + \text{unknown}^c$
		^f 652	.33	Partially melted.....	$\text{V}_2\text{O}_5^{\text{ss}}^d + \text{V}_2\text{O}_5 \cdot 9\text{Nb}_2\text{O}_5 + \text{unknown}^c$
		658	21do.....	Do.
		665	.33do.....	Do.
		^f 666	16	Partially melted.....	$\text{V}_2\text{O}_5^{\text{ss}}^d + \text{V}_2\text{O}_5 \cdot 9\text{Nb}_2\text{O}_5$
		670	.5do.....do.....
		674	.5do.....	$\text{V}_2\text{O}_5^{\text{ss}}^d + \text{V}_2\text{O}_5 \cdot 9\text{Nb}_2\text{O}_5$
		688	.5do.....do.....
		746	.5do.....	$\text{V}_2\text{O}_5^{\text{ss}}^d + \text{V}_2\text{O}_5 \cdot 9\text{Nb}_2\text{O}_5$
		828	1do.....	Do.
		902	1do.....	Do.
		961	4do.....	Do.
		1011	.5do.....	Do.
		1061	1do.....	Glass
		1096	.5	Completely melted.....	Do.

See footnotes at end of table.

TABLE 4. *Experimental data for compositions in the system vanadium oxide-niobium oxide—Continued*

Composition		Heat treatment ^a		Results	
V ₂ O ₅	Nb ₂ O ₅	Temp.	Time	Physical observation	X-ray diffraction analysis ^b
<i>Mole %</i>	<i>Mole %</i>	<i>°C</i>	<i>hr</i>		
80	20	1061	1	Partially melted	V ₂ O ₅ ^d _{ss} +V ₂ O ₅ ·9Nb ₂ O ₅
		1119	.75	do	Glass
		1140	.5	Completely melted	Do.
75	25	f 650	1	Partially melted	V ₂ O ₅ ^d _{ss} +V ₂ O ₅ ·9Nb ₂ O ₅
		f 690	16	do	Do.
		1061	1	Partially melted	Do.
		1130	.5	do	Glass+V ₂ O ₅ ·9Nb ₂ O ₅
		1154	.5	do	Glass
		1180	.33	Completely melted	
70	30	632	168	Not melted	V ₂ O ₅ +V ₂ O ₅ ·9Nb ₂ O ₅ +unknown ^c
		f 670	.5	Partially melted	V ₂ O ₅ ^d _{ss} +V ₂ O ₅ ·9Nb ₂ O ₅
		1064	.33	do	V ₂ O ₅ ^d _{ss} +V ₂ O ₅ ·9Nb ₂ O ₅
		1175	.5	do	V ₂ O ₅ ^d _{ss} +V ₂ O ₅ ·9Nb ₂ O ₅ +glass
		1204	.5	Melted ^h	Glass+unknown ^c
		1235	.5	do	Do.
		1246	.17	do	Do.
		1257	.5	do	Do.
66.67	33.33	1045	3	Partially melted	V ₂ O ₅ ^d _{ss} +V ₂ O ₅ ·9Nb ₂ O ₅ +unknown ^c
		1064	.66	do	V ₂ O ₅ ^d _{ss} +V ₂ O ₅ ·9Nb ₂ O ₅
65	35	g 637	.5	Not melted	V ₂ O ₅ +V ₂ O ₅ ·9Nb ₂ O ₅
		g 658	.5	Partially melted	V ₂ O ₅ ^d _{ss} +V ₂ O ₅ ·9Nb ₂ O ₅
		1062	24	do	Do.
		1175	.5	do	Do.
		1225	.5	Melted ^h	Do.
		1255	.75	do ^h	Do.
		1279	.5	do	Do.
		1280	.75	do	Do.
		f 654	1	Partially melted	
60	40	f 684	60	do	V ₂ O ₅ ·9Nb ₂ O ₅ +V ₂ O ₅ ^d _{ss}
		f 1014	60	do	Do.
		f 1062	24	do	Do.
		f 1100	65	do	Do.
		f 1219	.5	Melted ^h	V ₂ O ₅ ·9Nb ₂ O ₅ +V ₂ O ₅ ^d _{ss}
		f 1246	.17	do	V ₂ O ₅ ·9Nb ₂ O ₅ +V ₂ O ₅ ^d _{ss} +unknown ^c
		f 1277	.08	do	V ₂ O ₅ ·9Nb ₂ O ₅ +V ₂ O ₅ ^d _{ss}
55	45	1060	60	Partially melted	Do.
		1352	.17	Completely melted	
50	50	600	6	Not melted	V ₂ O ₅ ·9Nb ₂ O ₅ +V ₂ O ₅
		657	3	Partially melted	V ₂ O ₅ ·9Nb ₂ O ₅ +V ₂ O ₅ ^d _{ss}
		f 670	.5	do	
		f 688	.5	do	
		703	1	do	
		730	1	do	V ₂ O ₅ ·9Nb ₂ O ₅ +V ₂ O ₅ ^d _{ss}
		901	1	do	Do.
		999	16	do	Do.
		1049	22	do	Do.
		1092	1.5	do	Do.
		1300	.08	Melted ^h	Do.
		1358	.17	do	
		1382	.17	do	
		1402	.17	do	V ₂ O ₅ ·9Nb ₂ O ₅ +V ₂ O ₅ ^d _{ss}
45	55	1325	.1	do	
		1352	.1	do	
40	60	1324	.1	Melted ^h	
		1349	.1	do ^h	
30	70	963	.08	Partially melted	V ₂ O ₅ ·9Nb ₂ O ₅ +V ₂ O ₅ ^d _{ss}
		1119	.08	do	Do.
		1350	.08	Melted ^h	M—Nb ₂ O ₅ ⁱ ^e
		1375	.08	do ^h	Do.
		629	.25	Not melted	M—Nb ₂ O ₅ ⁱ +L Nb ₂ O ₅
		642	.33	do	
25	75	649	.5	Partially melted	V ₂ O ₅ ·9Nb ₂ O ₅ +V ₂ O ₅ ^d _{ss} +unknown ^c
		f 767	.3	do	V ₂ O ₅ ·9Nb ₂ O ₅ +V ₂ O ₅ ^d _{ss}
		880	16	do	Do.
		970	2	do	Do.
		g 1375	.08	do	
		g 1382	.08	do	
		g 1395	.08	Completely melted	
		g 1410	.25	do	L—Nb ₂ O ₅ ^j

See footnotes at end of table.

TABLE 4. *Experimental data for compositions in the system vanadium oxide-niobium oxide—Continued*

Composition		Heat treatment ^a		Results	
V ₂ O ₅	Nb ₂ O ₅	Temp.	Time	Physical observation	X-ray diffraction analysis ^b
<i>Mole %</i>	<i>Mole %</i>	<i>°C</i>	<i>hr</i>		
20	80	1006	24	Partially melted	V ₂ O ₅ :9Nb ₂ O ₅ +V ₂ O _{5ss} ^d
		1121	16	do	Do.
		1280	65	do	Do.
		1294	2	do	Do.
		1329	168	do	V ₂ O ₅ :9Nb ₂ O ₅ +V ₂ Nb ₂₃ O ₆₂
		1352	.66	do	V ₂ O ₅ :9Nb ₂ O ₅
		1377	2	do	V ₂ O ₅ :9Nb ₂ O ₅ +V ₂ Nb ₂₃ O ₆₂
		1394	.5	do	
		1410	.25	Completely melted	M-Nb ₂ O ₅ ⁱ
		1430	.25	do	Do.
15	85	1006	65	Partially melted	V ₂ O ₅ :9Nb ₂ O ₅
		1121	16	do	Do.
		1294	25	do	Do.
		1329	168	do	V ₂ Nb ₂₃ O ₆₂
		1400	1.5	do	V ₂ Nb ₂₃ O ₆₂ +Nb ₂ O _{5ss}
		1426	1.5	Completely melted	Do.
		1440	1.5	do	Do.
10	90	1000	65	Not melted	V ₂ O ₅ :9Nb ₂ O ₅
		1122	16	do	Do.
		1240	72	do	Do.
		1278	72	do	Do.
		1290	72	Partially melted	V ₂ O ₅ :9Nb ₂ O ₅ +V ₂ Nb ₂₃ O ₆₂
		1306	.08	do	Do.
		1311	72	do	V ₂ Nb ₂₃ O ₆₂ +V ₂ O ₅ :9Nb ₂ O ₅
		1311	72	do	V ₂ Nb ₂₃ O ₆₂
		1342	22	do	V ₂ O ₅ :9Nb ₂ O ₅ ^k
		1385	46	do	Nb ₂ O _{5ss}
		1431	.33	do	V ₂ Nb ₂₃ O ₆₂ +Nb ₂ O _{5ss}
		1441	2	do	M-Nb ₂ O ₅ ⁱ
		1455	1	Completely melted	Nb ₂ O _{5ss}
		1458	.33	do	M-Nb ₂ O ₅ +L Nb ₂ O ₅ ^j
		1471	.08	do	
9	91	1122	20	do	V ₂ O ₅ :9Nb ₂ O ₅ ^k
		1175	88	do	Do.
		1201	72	do	V ₂ O ₅ :9Nb ₂ O ₅ +X ^l
		1278	72	do	Do.
		1295	22	Partially melted	V ₂ O ₅ :9Nb ₂ O ₅
		1304	60	do	V ₂ Nb ₂₃ O ₆₂ +V ₂ O ₅ :9Nb ₂ O ₅
		1315	70	do	Do.
		1342	22	do	V ₂ O ₅ :9Nb ₂ O ₅
		1385	46	do	Nb ₂ O _{5ss} +V ₂ Nb ₂₃ O ₆₂
8	92	1006	65	Not melted	V ₂ O ₅ :9Nb ₂ O ₅ +X ^l
		1121	65	do	Do.
		1240	72	do	Do.
		1276	91	do	Do.
		1290	72	do	V ₂ Nb ₂₃ O ₆₂
		1297	25	do	(V ₂ O ₅ :9Nb ₂ O ₅ +X ^l +V ₂ Nb ₂₃ O ₆₂ +Nb ₂ O _{5ss}) ^e
		1307	90	do	V ₂ O ₅ :9Nb ₂ O ₅ +X ^l +V ₂ Nb ₂₃ O ₆₂) ^e
		1311	72	do	V ₂ Nb ₂₃ O ₆₂
		1350	24	Partially melted	V ₂ O _{5ss} :9Nb ₂ O ₅ +V ₂ Nb ₂₃ O ₆₂ +Nb ₂ O _{5ss}
		1389	19	do	Nb ₂ O ₅ +V ₂ Nb ₂₃ O ₆₂
7	93	1006	65	Not melted	(V ₂ O ₅ :9Nb ₂ O ₅ +M-Nb ₂ O ₅) ⁱ
		1175	88	do	(X ^l +Nb ₂ O _{5ss} +V ₂ Nb ₂₃ O ₆₂) ^e
		1201	72	do	(X ^l +V ₂ O ₅ :9Nb ₂ O ₅ +Nb ₂ O _{5ss}) ^e
		1229	72	do	Do.
		1283	4	do	X ^l +V ₂ O ₅ :9Nb ₂ O ₅
		1309	72	do	X ^l +V ₂ Nb ₂₃ O ₆₂
		1316	.5	do	(V ₂ Nb ₂₃ O ₆₂ +X ^l +Nb ₂ O _{5ss}) ^e
		1323	1	Partially melted	
		1323	72	do	V ₂ Nb ₂₃ O ₆₂ +V ₂ O ₅ :9Nb ₂ O ₅
		1329	168	do	V ₂ Nb ₂₃ O ₆₂ +X ^l
		1337	16	do	V ₂ O ₅ :9Nb ₂ O ₅ +Nb ₂ O _{5ss} +V ₂ Nb ₂₃ O ₆₂
		1450	.25	do	
6	94	1460	1	Completely melted	Nb ₂ O _{5ss} +X ^l
		1464	1	do	Nb ₂ O _{5ss} +X ^l +V ₂ Nb ₂₃ O ₆₂
		1006	16	Not melted	(V ₂ O ₅ :9Nb ₂ O ₅ +Nb ₂ O _{5ss}) ^e
		1121	65	do	(V ₂ O ₅ :9Nb ₂ O ₅ +X ^l +V ₂ Nb ₂₃ O ₆₂) ^e
		1240	72	do	Nb ₂ O _{5ss} +X ^l
		1297	25	do	(Nb ₂ O _{5ss} +V ₂ Nb ₂₃ O ₆₂) ^e
		1308	70	do	Nb ₂ O _{5ss} +X ^l
		1389	.06	do	
		1397	17	Partially melted	Nb ₂ O _{5ss}
		1403	.06	do	

See footnotes at end of table.

TABLE 4. Experimental data for compositions in the system vanadium oxide-niobum oxide—Continued

Composition		Heat treatment ^a		Results	
V ₂ O ₅	Nb ₂ O ₅	Temp.	Time	Physical observation	X-ray diffraction analysis
<i>Mole X</i>	<i>Mole X</i>	<i>°C</i>	<i>hr</i>		
5	95	≐ 1006	65	Not melted	(M-Nb ₂ O ₅ ⁱ +V ₂ O ₅ ·9Nb ₂ O ₅) ^e
		≐ 1175	88	do	V ₂ O ₅ ·9Nb ₂ O ₅ +X ^l
		≐ 1201	72	do	V ₂ O ₅ ·9Nb ₂ O ₅ +X ^l
		≐ 1229	72	do	Nb ₂ O ₅ _{ss} ^m
		≐ 1295	2	do	Do.
		≐ 1308	70	do	Do.
		≐ 1397	16	do	Do.
		≐ 1412	.25	do	
		≐ 1427	.25	Partially melted	
		≐ 1460	.25	do	Nb ₂ O ₅ _{ss} +X ^l
4	96	≐ 1006	65	Not melted	L-Nb ₂ O ₅ +Nb ₂ O ₅ _{ss} ^m
		≐ 1121	65	do	Nb ₂ O ₅ _{ss} ^m
		≐ 1236	115	do	Do.
		≐ 1296	25	do	Do.
		≐ 1308	70	do	Do.
3	97	≐ 1233	72	do	Do.
		≐ 1405	.25	do	
		≐ 1420	.16	do	
		≐ 1455	.16	do	
		≐ 1457	.16	Partially melted	
		≐ 1472	.06	do	
		≐ 1477	.16	Completely melted	
2	98	≐ 1236	115	Not melted	Nb ₂ O ₅ _{ss} ^m
		≐ 1296	25	do	Do.
1	99	≐ 1233	72	do	Do.

^a All specimens were preheated to 500 °C for 10 hr. Rate of heating and cooling was approximately 3°/min. Specimens were heated in sealed Pt tubes and quenched from temperature indicated.

^b The phases identified are given in the order of the amount present (greatest amount first) at room temperature. These phases are not necessarily those present at the temperature to which the specimen was heated.

^c Unknown—a small amount of an unknown metastable phase with x-ray diffraction lines occurring at the following 2θ values: 22.22°, 27.27°, 30.28°, 37.84°, 44.78°, 45.22°, 47.34°, and 49.70°.

^d Specimen contained metastable "V₂O₅ type solid solution" when quenched from above the solidus and examined at room temperature.

^e The interpretation of the x-ray diffraction pattern is inconsistent with the phase diagram and is considered to be non-equilibrium due to differences in time and/or temperature of heat treatment.

^f Second heat treatment was 600 °C for 168 hr in sealed Pt tubes. Rate of heating and cooling was approximately 3°/min.

^g Second heat treatment was 1000 °C for 5 hr. Rate of heating and cooling was approximately 3°/min.

^h Criteria could not be established to determine complete melting (see sec. 2).

ⁱ Specimen contained (nonequilibrium) M-type Nb₂O₅ [29].

^j Specimen contained (nonequilibrium) low temperature form of Nb₂O₅ when quenched from above the liquidus and examined at room temperature.

^k The presence of a second phase was detected with a petrographic microscope.

^l Unknown phase occurring at about 93 to 94 mole percent Nb₂O₅.

^m Specimen contained a phase interpreted as Nb₂O₅ solid solution, however; other discrete phases may be present which are not detected by the present experimental methods.

4.1. Description of Phase Diagram

The liquidus falls sharply from the melting point of V₂O₅ (675 °C) to a eutectic at about 1 mole percent Nb₂O₅ and 648 °C. The exact eutectic composition was not determined because of the relatively small amount of Nb₂O₅ involved and the liquidus lines defining the eutectic composition are dashed. The liquidus is also dashed from 30 to 70 mole percent Nb₂O₅ (see sec. 2) and is indicated as rising smoothly from the eutectic composition to a peritectic at about 48 mole percent Nb₂O₅ and 1290 °C which corresponds to the incongruent melting temperature of the compound V₂O₅·9Nb₂O₅. There is no apparent solid solution on either side of this compound, as indicated by the similarity of unit cell dimensions in the two phase regions adjacent to the 1:9 composition. The liquidus again rises smoothly to another peritectic at about 57 mole percent Nb₂O₅ and 1322 °C which represents the incongruent melting temperature of the compound V₂Nb₂₃O₆₂.

A two phase area should separate the compounds V₂Nb₂₃O₆₂ and V₂O₅·9Nb₂O₅. This small area, represented in figures 1 and 2 as extending in width from 90 to 92 mole percent Nb₂O₅, was not found experimentally and is dashed. The liquidus rises again from approximately 60 mole % Nb₂O₅ and 1332 °C, the incongruent melting point of the phase occurring at some composition apparently between 93 and 94 mole percent Nb₂O₅ to the melting point of Nb₂O₅.

A narrow two phase area was found to occur from about 92 to 94 mole percent Nb₂O₅ separating the X compound and the 2V₂O₅·23Nb₂O₅ compound. Another two phase area, of less than 1 mole percent width just below the solidus, separates the X compound and Nb₂O₅ ss field. About 5 mole percent V₂O₅ is apparently accepted by Nb₂O₅ in solid solution. Since the unit cell dimensions of the Nb₂O₅ solid solution did not change significantly with composition, the solid solution area was delineated by the disappearing phase method. In addition, it should again be emphasized at this

point, that the x-ray diffraction patterns for $2V_2O_5 \cdot 23Nb_2O_5$ and the X compound bear a marked similarity to one another and to the high temperature form of Nb_2O_5 . Furthermore, it is not impossible that other discrete phases may exist which are below the limit of detection of the experimental conditions employed.

Since V_2O_5 did not stabilize the low temperature form of Nb_2O_5 and since temperatures below 1200 °C were not sufficient to attain equilibrium, the lines delineating the areas represented on figure 1 from 90 to 99 mole percent Nb_2O_5 (below 1200 °C) were dashed.

The liquidus rises again from 1332 °C and 60 mole percent Nb_2O_5 , the peritectic for the X compound to the melting point of Nb_2O_5 . This 1485 °C melting point was determined previously by the authors [22] and was not redetermined for this study.

4.2. Reversibility, Oxidation, and Reduction

Relatively long periods of time at temperatures above the apparent minimum decomposition temperature of 1288 °C were required in order to form the $2V_2O_5 \cdot 23Nb_2O_5$ compound. This apparent minimum decomposition was delineated from data obtained by heating the compound at successively higher temperatures.

To establish reversibility, it is necessary to decompose the compound into the same two phases previously seen below the apparent minimum decomposition temperature. Both the 92 and 93 mole percent Nb_2O_5 compositions were reheated at lower temperatures in sealed and unsealed Pt tubes and these results are given in table 5. The composition 8 mole percent V_2O_5 :92 mole percent Nb_2O_5 when heated to 1307 °C for 90 hr in a sealed Pt tube

formed the compound $V_2Nb_{23}O_{62}$. This compound when reheated in a closed Pt tube at 1222 °C for 70 hr as outlined in table 5 was not reversed to $V_2O_5 \cdot 9Nb_2O_5 + X$ phase, but formed only the X phase at the expense of some $V_2Nb_{23}O_{62}$. This X phase apparently exists at some composition between 93 and 94 mole percent Nb_2O_5 . A portion of the same specimen previously heated 1222 °C for 70 hr was again reheated to 1298 °C for 68 hr in a sealed Pt tube and further reduction apparently took place. Some of the $V_2Nb_{23}O_{62}$ was still present but the X phase could no longer be detected. Another more reduced phase occurred which was found from x-ray diffraction data to be apparently isostructural with the compound $Ti_2Nb_{10}O_{29}$ reported by Wadsley [23].

The situation, however, is quite different when the same composition received a similar heat treatment in unsealed Pt tubes. When the compound $V_2Nb_{23}O_{62}$, previously formed by heating to 1307 °C for 90 hr was reheated at 1222 °C for 70 hr in an unsealed tube, the x-ray diffraction powder pattern data indicated that the specimen apparently contained a non-equilibrium mixture of three phases, the X phase, $V_2O_5 \cdot 9Nb_2O_5$, and $V_2Nb_{23}O_{62}$. Apparently it was approaching binary equilibrium and tending to reverse into $V_2O_5 \cdot 9Nb_2O_5 + X$ phase. A portion of this material previously heated at 1222 °C for 70 hr unsealed was again reheated to 1298 °C for 68 hr in an open tube. The x-ray diffraction pattern of this material showed the presence of 2 phases $2V_2O_5 \cdot 23Nb_2O_5$ and X phase. It has apparently changed composition slightly due to volatilization.

In view of the foregoing discussion of an open versus closed system, it can probably be concluded that in the V_2O_5 - Nb_2O_5 system, specimens when

TABLE 5. Experimental data for reversibility of phases in the system vanadium oxide-niobium oxide

Composition Mole %		Initial heat treatment		X-ray ^a	Final heat treatment		X-ray ^a
V_2O_5	Nb_2O_5	Temp.	Time	Identification	Temp.	Time	Identification
		°C	hr		°C	hr	
7	93	500	10				
		1000	5				
		^b 1323	72	$X^c + V_2O_5 \cdot 9Nb_2O_5$ -----	^b 1235	72	X ^c
		500	10				
		1000	5				
		^b 1323	72	$X^c + V_2O_5 \cdot 9Nb_2O_5$ -----	^b 1219	144	$X^c + V_2O_5 \cdot 9Nb_2O_5$
8	92	500	10				
		^b 1307	90	$2V_2O_5 \cdot 23Nb_2O_5$ -----	^b 1298	168	$2V_2O_5 \cdot 23Nb_2O_5$
		500	10				
		^b 1307	90	$2V_2O_5 \cdot 23Nb_2O_5$ -----	^b 1222	70	$2V_2O_5 \cdot 23Nb_2O_5 + X^c$
		500	10				
		^b 1307	90	$2V_2O_5 \cdot 23Nb_2O_5 + X^c$ -----	^b 1298	68	$2V_2O_5 \cdot 23Nb_2O_5 + (V,Nb)_{12}O_{29}^{d1}$
		^b 1222	70				
		500	10				
		^b 1307	90	$2V_2O_5 \cdot 23Nb_2O_5$ -----	^c 1222	70	$X^c + V_2O_5 \cdot 9Nb_2O_5 + 2V_2O_5 \cdot 23Nb_2O_5$
		500	10				
		^c 1307	90				
		^c 1222	70	$X^c + V_2O_5 \cdot 9Nb_2O_5 + 2V_2O_5 \cdot 23Nb_2O_5$ -----	^c 1298	68	$2V_2O_5 \cdot 23Nb_2O_5$

^a The phases identified are given in the order of amount present (greatest amount first) at room temperature. The phases are not necessarily those present at the temperature to which the specimens were heated.

^b Specimen heated in sealed Pt tube and quenched.

^c Unknown phase occurring in the system at approximately 93 to 94 mole percent Nb_2O_5 .

^{d1} A reduced phase apparently isostructural with the monoclinic form of $2TiO_2 \cdot 5Nb_2O_5$ [23].

^e Specimen heated in open Pt tube and quenched.

heated in a closed or oxygen deficient environment tended to reduce with time and those heated in an open or oxygen rich environment tended to reverse and approach binary equilibrium. Since the experimental evidence apparently did not validate reversibility in the closed or restricted oxygen situation, the line indicating a minimum decomposition for the compound $V_2Nb_{23}O_{62}$ was dashed.

5. Nb_2O_5 -Type "Solid Solution"

A re-examination of selected compositions in the systems $ZnO-Nb_2O_5$; $NiO-Nb_2O_5$; $Al_2O_3-Nb_2O_5$; $TiO_2-Nb_2O_5$; and $ZrO_2-Nb_2O_5$, has shown that phases reported previously as " Nb_2O_5 solid solution" are, in fact, discrete compounds. Several of the compounds in the $V_2O_5-Nb_2O_5$ pseudo-binary system (VNb_9O_{25} , $V_2Nb_{23}O_{62}$ and $(V, Nb)_{12}O_{29}$) have apparently analogous structures in other mixed oxide systems.

All of these phases are grouped in table 6 into five general formula types according to the cation to anion ratio.

It is worth noting that in this investigation no phase was detected in the $V_2O_5-Nb_2O_5$ pseudo-binary system with either of the cation to anion ratios 11:27 or 3:7.

Goldschmidt [3] reported the existence of $Nb_2O_{5.88}$ in the $Al_2O_3-Nb_2O_5$ system. Thereafter, Layden [24] postulated from the Norin and Magneli [25] formulae that compounds should occur at the compositions $Al_2O_3 \cdot 9Nb_2O_5$, $Al_2O_3 \cdot 25Nb_2O_5$ and $Al_2O_3 \cdot 49Nb_2O_5$ but found only the first two. Roth, Wadsley & Gatehouse [26] reported the compound $Al_{1/3}Nb_{24/3}O_{62}$ (1:49) and indicated, from structural considerations, that the 1:25 compound should have the composition $AlNb_{21}O_{54}$. Andersson and Roth [27] from single crystal data found the compound occurring around the 1:9 composition to have the actual formula $Al_2O_3 \cdot 11Nb_2O_5$.

6. Summary

The system $V_2O_5-Nb_2O_5$ was studied and the phase diagram was constructed from fusion characteristics, and x-ray diffraction data.

From structural considerations and from experimental evidence this system does not appear to be binary.

There seemed to be no evidence for equilibrium solid solution of Nb_2O_5 in V_2O_5 and a eutectic occurred at approximately 1 mole percent Nb_2O_5 and 648 °C.

The existence of three intermediate compounds was postulated. The first, $V_2O_5 \cdot 9Nb_2O_5$ melted incongruently at about 1290 °C and the second $V_2Nb_{23}O_{62}$ melted incongruently at about 1322 °C. The third compound which melted incongruently at about 1332 °C was found to exist at some composition between about 93 and 94 mole percent Nb_2O_5 . Up to about 5 mole percent V_2O_5 was apparently accepted by Nb_2O_5 in solid solution lowering the melting point of Nb_2O_5 from 1485 to 1332 °C.

The possibility of other discrete phases which cannot be identified by the experimental techniques employed in the study must not be excluded in the region from 90 to 99 mole percent Nb_2O_5 . In addition the Nb_2O_5 rich portions of the following binary systems were reinvestigated: $ZnO-Nb_2O_5$, $NiO-Nb_2O_5$, $Al_2O_3-Nb_2O_5$, $TiO_2-Nb_2O_5$, and $ZrO_2-Nb_2O_5$. Solid solution of M_xO_y with Nb_2O_5 was previously reported in all cases in excess of 90 mole percent Nb_2O_5 . Subsequent data (table 6) has shown that in each of these systems discrete compounds could be identified in compositions previously reported as being Nb_2O_5 solid solution. The compound $V_2Nb_{23}O_{62}$ is apparently isostructural with $TiNb_{24}O_{62}$ and $AlNb_{24/3}O_{62}$. The highly reduced compound $(V,Nb)_{12}O_{29}$ is apparently isostructural with $Ti_2Nb_{10}O_{29}$, $Nb_{12}O_{29}$, $AlNb_{11}O_{29}$, $NiNb_{11}O_{29}$, and $ZnNb_{11}O_{29}$.

TABLE 6. Apparently isostructural phases in mixed oxide systems of Nb_2O_5 or Ta_2O_5

Composition	Valence of cation additions to Nb_2O_5 and/or Ta_2O_5			
	Cation: Anion	$M_2O_5-M'_2O_5$	$M_2O_5-M'_2O_5$	$M_2O_5-M'_2O_5$
2:5		Nb_2O_5 VNb_9O_{25} ^a [13] $P Nb_9O_{25}$ [13] $As Nb_9O_{25}$ [13] $Ta_{3/3}Nb_{6/3}O_{25}$ [13] $P Ta_9O_{25}$ [13] $As Ta_9O_{25}$ [13] $V Ta_9O_{25}$ [13]	$GeO_2 \cdot 9Nb_2O_5$ ^b [13]	
25:62		$V_2Nb_{23}O_{62}$ ^c + $\frac{1}{2}O$	$TiNb_{24}O_{62}$ ^d [1, 16] $ZrNb_{24}O_{62}$ ^d [1]	$Al_{1/2}Nb_{24/2}O_{62}$ [26]
11:27		$[NbO_2 \cdot 46]$ [25] $[NbO_2 \cdot 467]$ [28] $[NbO_2 \cdot 451]$ [26]		$Al_2O_3 \cdot 25Nb_2O_5$ [24] $Al_{1/2}Nb_{10/2}O_{27}$ [26]
12:29		$(V,Nb)_{12}O_{29} + O$ ^c	$Ti_2Nb_{10}O_{29}$ [23]	$AlNb_{11}O_{29}$ [26] [27] $Ni_{2/3}Nb_{11/3}O_{29}$ [26] $Zn_{2/3}Nb_{11/3}O_{29}$ ^e
3:7		$TiNb_2O_7$ [23]		

^a This phase was previously reported as solid solution [3] (see sect. 3).

^b Ge^{+4} is accepted into the structure and would seem to indicate that either the cation/anion ratio is varying or that minor differences exist in the packing of cation coordination polyhedra.

^c This phase has not been previously reported in the binary system.

^d This phase was originally reported as solid solution [1] but later described as a compound by one of the authors [16].

^e This phase previously unreported is apparently isostructural with the high temperature polymorph of $Ti_2Nb_{10}O_{29}$ and has the following unit cell dimensions: $a=15.57$ Å, $b=3.826$ Å, $c=20.5$ Å and $\beta=113^\circ 41'$.

7. References

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